



**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Application No.L : 10/026,171 Confirmation No. 9429  
Applicants: : Agapiou *et al.*  
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Examiner: : James E. McDonough  
  
Docket No.: : 1999U024.D1.US  
Customer No.: : 25959

**Commissioner for Patents  
Mail Stop Amendments  
P. O. Box 1450  
Alexandria, VA 22313-1450**

**SUPPLEMENTAL DECLARATION UNDER 37 CFR § 1.132**

Sir:

I, Agapios K. Agapiou, declare as follows:

I am a co-inventor of the description and all the claimed subject matter in the above referenced patent application. The purpose of this Declaration is to demonstrate that the claims describing heating techniques used in the reaction between metallocenes and methyl alumoxane (MAO) resulted in unexpected and surprising improvement (lowering) of reactor fouling and maintenance or improvement in catalyst activity, when compared to no added heat during the reaction between the metallocenes and MAO. The techniques claimed, furthermore, are not disclosed in either WO 96/35729 or US 5,914,289 (Razavi I or II). In the examination of the above referred patent application, the Examiner relies on these two references, Razavi I and/or Razavi II, in rejecting the claims. Under my direction and control, a series of experiments was conducted to evaluate the catalyst preparation techniques of these two references and compare these reference techniques to our claimed techniques.

## **Catalyst Preparation Comparing Univation and Razavi I&II Methods**

### **Univation Catalyst Preparation**

Weigh 0.123 g of dimethylsilyl-bis(tetrahydroindenyl) zirconium dichloride (Boulder Scientific) into a 125 ml hypovial. Add 20 ml of dried/degassed toluene and a magnetic stir bar to the vial. Add 6.2 g of a 30 wt% methylaluminoxane in toluene solution (Albemarle). Place the hypovial in an 85°C oil bath and stir/react for 15 minutes. Add 5.0 g of Davidson 955 silica gel that has been dehydrated at 600°C. React/stir for 15 minutes at 80°C. Dry under N<sub>2</sub> purge at 80°C until the powder becomes free-flowing. The final catalyst is pale yellow and weighs 7.0 g.

### **Razavi I & II Catalyst Preparation**

Weigh 0.123 g of dimethylsilyl-bis(tetrahydroindenyl) zirconium dichloride into a 125 ml hypovial. Add 20 ml of dried/degassed toluene and a magnetic stir bar to the vial. Add 6.2 g of 30 wt% methylaluminoxane in toluene solution. The mixture was reacted and stirred for 10 minutes at ambient temperature (20°C). Add 5.0 g of Davidson 955 silica gel that has been dehydrated at 600°C. React/stir for 5 minutes at ambient temperature (20°C). Place the vial containing the catalyst slurry in a 110°C oil bath and react/stir for 90 minutes. Dry the final catalyst at 110°C under a N<sub>2</sub> purge until it becomes a free-flowing powder. Final catalyst is pale yellow and weighs 7.0 g.

### **Polymerization Reactor Conditions for Evaluation of Univation and Razavi I & II Catalysts**

Catalysts were polymerized in a 2-liter Zipperclave® reactor. The reactor was cleaned and purged with dry N<sub>2</sub> at 100°C. It was then cooled to 30°C under a N<sub>2</sub> purge and a catalyst injection tube with 100 mg of the desired catalyst was attached to the reactor. The reactor was pressure / purged 3 times with ethylene and vented to 5 psig. Via a syringe, 20 ml of dried/degassed 1-hexene was added to the reactor. Via syringe, 0.3 ml of a 0.5 M solution of tri-ethyl aluminum/hexane was added to the reactor. 800 ml of iso-butane was pressured into the reactor as a diluent for the polymerization. The reactor was heated and the agitator speed set at 1000 RPM. After the reactor internal temperature reached 83°C, the catalyst was pressured into the reactor with ethylene at 325 psig. The reaction was run at 85°C for 40 minutes at 325 psig. The ethylene uptake in liters/ minute and the jacket and internal temperatures were recorded by a

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data acquisition system. The final yield was determined after drying the polymer in a vacuum oven and weighing the cooled resin. Notes and photos about fouling characteristics of each polymer are included in the accompanying documentation of the runs.

As table 1 and the photos clearly indicate, pre-heating the metallocene/MAO mixture prior to heating it with silica is critical to obtaining the improved (lower) fouling and (higher) catalyst activity performance. A catalyst was made (00277-132-2) using the standard conditions for the examples in the Razavi documents (no pre-heating of the metallocene/MAO mixture, but heating the metallocene/MAO/silica mixture at 110°C for 90 minutes) and polymerized in a 2.2 liter autoclave reactor. The resulting polymer fouled the reactor badly (see photos 78 & 79, attached, corresponding to polymerization runs 00311-78 & 00311-79 respectively). When a catalyst was made in run 00311-80 using identical reagents to the ones in the above example but with pre-heating the metallocene/MAO mixture prior to silica deposition/reaction(as presently claimed), the resulting polymer after polymerization at identical conditions exhibited granular morphology and no fouling was observed (photo 80).

We believe that the importance of the pre-heating step (our invention) is paramount to obtaining a non-fouling catalyst when using bridged metallocenes because driving the sparingly soluble metallocene reaction with MAO to the complete ion pair, allows the totally soluble catalyst component to stay chemically attached to the support and thus prevent fouling.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 or Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above-referenced application or an patent issuing therefrom.

Respectfully submitted,

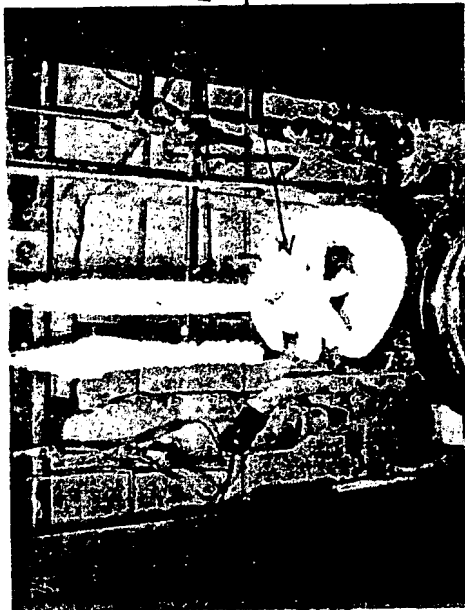
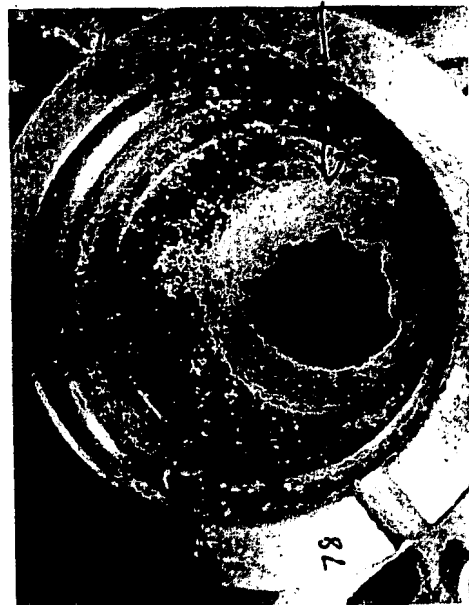
September 7, 2007.  
Date

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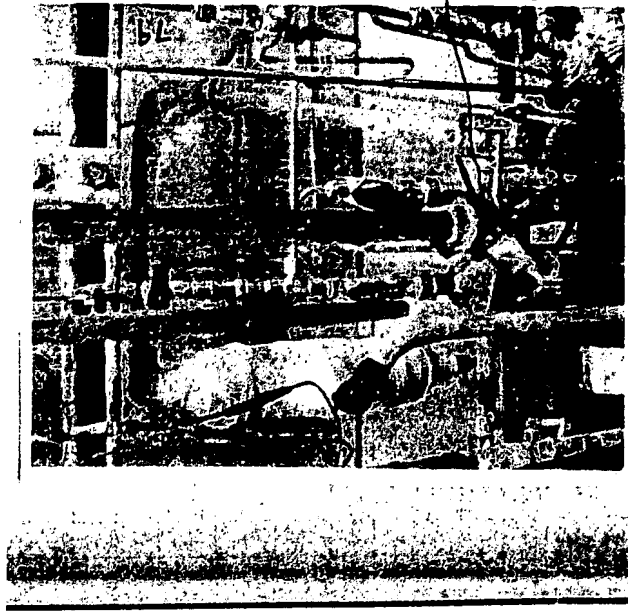
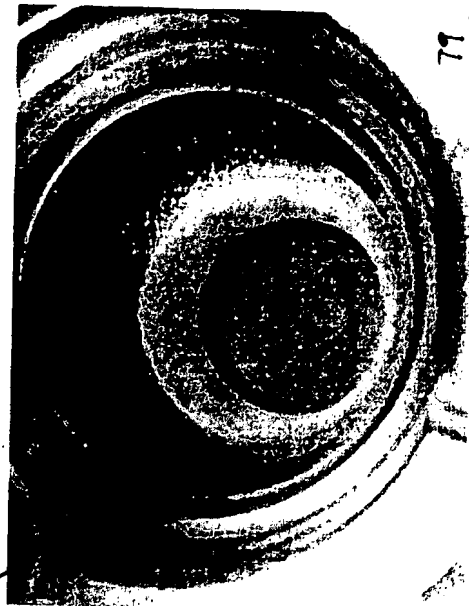
**Run 00311-078 Using Catalyst Prepared by Fina Method**

No Antifoulant



**Run 00311-079 Using Catalyst Prepared by Fina Method**

Antifoulant was presented during the polymerization test



Run 00311-080 Using Catalyst Prepared with Univation Method

No Antifoulant

